The Steady States of an Electron in a Phonon-Modulated Lattice

by

William Bend
The Department of Physics
The State College of Washington
Pullman Washington

Prepared May 18th 1953 as a technical report of work done under contract N7-onr-33005 of project NR 010-603 and distributed according to the list for that project

Abstract

An electron in a lattice potential together with the phonon modes of the lattice are treated as a single combined system for which the wave functions are products of Bloch functions for the electron and Hermite polynomial oscillator functions for the normal modes of the lattice vibrations. The classical oscillatory motion of the lattice points is replaced by the probability distributions of the oscillator wave functions, and the modulation of the lattice potential by the phonon modes depends only on the electron position coordinates and on the generalized coordinates of the phonon modes - it does not depend explicitly on the time.

Steady "resonance" states of the combined system, electron plus phonon, are shown to exists in which a single quantum of phonon energy passes back and forth between electron and lattice, the total energy is conserved, and the normalization of the combined eigenfunction is a constant independent of time. The electric current carried in these steady states can have any arbitrary value, and the phonon modulated lattice has absolutely zero resistance.

Electrical resistance is considered due to random transitions among the phonon oscillator states of the lattice, stimulated by thermal fluctuations, and the significance of this for the theory of superconductivity is briefly discussed.

Introduction

Consider some quantum mechanical problem with a Hamiltonian H_o whose eigenfunctions are known. Let the Hamiltonian be perturbed to H with unknown eigenfunctions. The standard procedure is to look for these unknown eigenfunctions in the form of linear combinations of the unperturbed eigenfunctions of H_o, with coefficients that may be functions of the time. If the system is initially prepared in one of the unperturbed states, the perturbation switch on at time zero, and switched off again at time t, the square modulus of any one of the coefficients equals the probability that the corresponding eigenvalue be found by an observation made after time t.

When however the perturbation is essentially a difference between the true Hamiltonian H and an arbitrary but convenient H_o, and is present permanently, one is not free to use the coefficients to calculate transition probabilities between the unperturbed states, which are in this case purely fictitious.

This is specially important when the Hamiltonian H contains time explicitly. For example one may consider a lattice potential perturbed by an elastic vibration. The conventional calculation then gives the transition probabilities for an electron to make jumps from one eigenstate of the unperturbed lattice to another, due to the perturbation, the energy difference being taken care of by the acoustical energy quanta. This is in fact the basis of the standard theory of electrical resistance. But

if the elastic vibration is a standing wave, i.e. a permanent feature of the problem, these transition probabilities are purely fictitious, because the electron cannot be prepared in an eigenstate of the unperturbed lattice in the first place, the elastic vibration switched on at time zero and off again prior to the next measurement. The vibration is present all the time and the electron must be in a state appropriate to this more complicated field.

The correct picture must be developed as follows: the system includes both electron and lattice with its spectrum of normal modes. The Hamiltonian of this system involves three terms: the electron, the phonons, and the interaction between them that occurs because of the phonon modulation of the lattice potential. Any wave function for such a Hamiltonian is a product of two factors: (i) a function of the electron coordinates and time, and (ii) a function of the generalized coordinates of the normal modes and time. The resulting eigenfunctions of the complete Hamiltonian turn out to be resonance states in which energy passes between the electron and the phonons in an oscillatory fashion with no net accumulation in either part. The square modulus of such an eigenfunction is independent of time and it represents a true steady state of the complete system, electron plus phonons. It is not necessary for the net current to vanish in order to set up these steady states, and the phonon modulated lattice offers no resistance to current-carrying states.

In a natural crystal switches continually occur. Under thermal bath

conditions, the quantum state of the phonons is being changed in a random manner; these random changes in the normal modes are exactly the feature that distinguishes thermal motion from acoustical vibrations that arise from a coherent source. An externally stimulated transition in the phonon state of the lattice - stimulated by a temporary perturbation from the thermal bath - will induce transitions in the electron states and give rise to resistance. These switches however are from one phonon modulated state to another, not from one unmodulated lattice state to another. In the new picture one has to prepare the combined system in one of the phonon modulated states, then switch on the thermal perturbation and calculate transition probabilities to the steady states in the new phonon modulation.

In this paper we first develop the general formalism far enough to prove the existence of steady current-carrying states in the coherent phonon modulated lattice. Then we give an approximate theory which may turn out to be more useful in later applications of these new concepts to the detailed theory of resistence and superconductivity. The theory of transitions induced by thermal perturbations of the phonon modulations is reserved for a later paper.

The steady states of the phonon moduleted lattice

To deacribe the combined system, electron plus phonon, we shall use for the electron, eigenfunctions $u_k(q)$ in an ideal lattice with a Hamiltonian H_o and eigenvalues E_k, writing a linear combination of these functions for the electron factor in the combined wave function. For the phonons we use the normal modes of the lattice. The displacement of a lattice point at normal position q due to the p^{th} normal mode is classically

$$Y_p(q) = A_p e^{iw_p t} \cos(\pi p q/L) \qquad (1)$$

where w_p is the angular frequency of the p^{th} mode, and the cosine factor is understood to be a product of three cosines, one for each dimensions of the crystal of side L. The coefficients

$$y_p(t) = A_p e^{iw_p t} \qquad (2)$$

are generalized coordinates for the phonon motion, and the classical Hamiltonian in terms of these coordinates is well known:

$$H_{phon} = \tfrac{1}{2}\sum_p \dot{y}_p^2 + \tfrac{1}{2}\sum_p y_p^2 w_p^2 \qquad (3)$$

To be consistent, the theory must now treat the phonon part of the problem by replacing the Hamiltonian (3) by an operator and seek its eigenfunctions:

$$H_{phon}\,\phi = -\tfrac{1}{2}\hbar^2 \sum_p \partial^2\phi/\partial y_p^2 + \tfrac{1}{2}\sum_p w_p^2 y_p^2 \phi = E_{phon}\,\phi \qquad (4)$$

The eigenfunctions for this operator are clearly products of the familiar Hermite polynomial eigenfunctions of the simple harmonic oscillator, one for each normal mode coordinate, the eigenvalues being sums of $(n+\tfrac{1}{2})\hbar w_p$.

$$\phi(\{n\},\{y\},t) = \prod_p N_{np}\, e^{-\frac{1}{2}\alpha_p y_p^2}\, H_{np}(\sqrt{\alpha_p}\, y_p)\, e^{i(n_p+\frac{1}{2})w_p t} \qquad (5)$$

where $\alpha_p = w_p/\hbar$ and N_{np} are normalization constants. This function depends on all the normal coordinates y_p, and the state is specified by the set $\{n\}$ of quantum numbers n_p, one number for each mode.

Coupling between the electron and phonons is secured through the phonon modulation of the lattice potential. If the phonon amplitudes are not too great, the potential modulation is proportional to the relative displacements of the lattice points, so that we may write for this potential modulation:

$$V = \sum_p K_p\, y_p \sin(\pi pq/L) \qquad (6)$$

where again a product of three sines is understood, q is the electron coordinate, and y_p the normal mode coordinate that appears also in eqs. (2) - (5). Note that V is not a function of time explicitly.

The combined Hamiltonian is now

$$H = H_o + H_{phon} + V \qquad (7)$$

and we seek eigenfunctions of this Hamiltonian having the form

$$\Psi(\{y\},q,t) = \sum_{\{n\}}\sum_k C(k,\{n\},t)\, u_k(q)\, e^{-iE_k t/\hbar}\, \phi(\{n\},\{y\},t) \qquad (8)$$

where the "constants" $C(k,\{n\},t)$ have to be determined. Writing this function into the Schrodinger equation

$$H\Psi = i\hbar\, \partial\Psi/\partial t \qquad (9)$$

and cancelling identical terms due to the fact that the ϕ are eigenfunctions of H_{phon} and the u's are eigenfunctions of H_o, one obtains, after the usual steps familiar in the method of variation of constants:

$$i\hbar dC(j,\{m\},t)/dt = \sum_{\{n\}}\sum_{k}\iint \bar{\phi}(\{m\},\{y\})\,\bar{u}_j(q)\,V\,u_k(q)\,\phi(\{n\},\{y\})\,dq\prod_p dy_p$$

$$\times\ C(k,\{n\},t)\exp\left\{i\left[E_j - E_k + \sum_p (m_p - n_p)w_p\hbar\right]t/\hbar\right\} \qquad (10)$$

where $\phi(\{n\},\{y\})$ etc., means the function (5) without its time factor.

We can seek solutions for the coefficients of the form

$$C(j,\{m\},t) = C(j,\{m\})\exp\left[-2\pi i W(j,\{m\})t\right] \qquad (11)$$

where $C(j,\{m\})$ and $W(j,\{m\})$ are constants. Eq.(10) then becomes

$$\sum_k\sum_{\{n\}}\left[(\{m\},j|V|k,\{n\})\exp\left\{i\left[E_j - E_k + \sum_p (m_p - n_p)\hbar w_p\right]t/\hbar\right\}\right.$$

$$\left. - hW(k,\{n\})\,\delta_{kj}\delta_{\{m\}\{n\}}\right]C(k,\{n\},t) = 0 \qquad (12)$$

where the V-matrix is an obvious abbreviation. These equations are soluble for the coefficients C in the following way. First we take all the constants $W(k,\{n\})$ the same, independent of the state $(k,\{n\})$, cancel the time factor of $C(k,\{n\},t)$ in eq.(12). We then accept non-zero coefficients $C(k,\{n\})$ only for those states such that between any pair for which the matrix of V is not zero, the energy is conserved:

$$E_j - E_k + \sum_p (m_p - n_p)\hbar w_p = 0 \qquad (13)$$

Eq.(12) for the non-vanishing coefficients then becomes

$$\sum_k \sum_{\{n\}} \left[(\{m\}, j|V|k, \{n\}) - \hbar W \delta_{kj} \delta_{\{m\}\{n\}} \right] C(k, \{n\}) = 0 \qquad (14)$$

This is soluble when W is one of the eigenvalues of the V-matrix, and because the latter does not contain time, the solutions are indeed constants.

Inspection of the V matrix shows that it vanishes identically unless for one and only one normal mode, the p^{th}, $m_p = n_p + 1$ or $n_p - 1$. This is because V is summed over all the normal modes, while the integration is a product over the modes, each multiple integral containing as a factor in the integrand only one normal coordinate y_p from the p^{th} term in V. To satisfy eq.(13) therefore the states j and k must be such that

$$E_j - E_k = \pm \hbar w_p \quad \text{for some } p \qquad (15)$$

At the same time, non-vanishing if the V matrix element requires that the integral

$$\int \bar{u}_j(q) \sin(\pi pq/L)\, u_k(q)\, dq \neq 0 \qquad (16)$$

These two conditions are sufficient in general to determine the energies E_j and E_k for any given mode p. Eq.(15) is of course the conservation of energy during electron-phonon interaction, while eq.(16) turns out to be conservation of momentum between phonon and electron.

As the simplest example, we can form the function (8) from one pair of Bloch functions, with k and j the wave numbers for the electron states. The V-matrix is then a four-by-four Hermitian matrix with all elements zero except those on the anti-diagonal, its eigenvalues turn out to be $\pm V(n,p)$

where $$V(n,p) = (K_p/\alpha_p 2^{\frac{1}{2}})\sqrt{\tfrac{1}{2}(n+1)} \qquad (17)$$

From a classical point of view these are the amplitudes of the potential wave (8) having n quanta of energy. If the velocity of propagation of phonon waves in the lattice is c, we have

$$w_p = 2\pi pc/L \qquad (18)$$

and the conservation eqs.(15) and (16) yield*

$$\left.\begin{aligned} k &= \tfrac{1}{2}p \pm mLc/h \\ j &= -\tfrac{1}{2}p \pm mLc/h \end{aligned}\right\} \qquad (19)$$

where m is the effective mass of the electron. The positive signs correspond to positive current, the lower signs to negative current, the sign of the current being arbitrary. Taking positive current only, there are two functions (8) corresponding respectively to the two eigenvalues of $\pm V(n,p)$:

$$\Psi_p = (1/2^{\frac{1}{2}})(u_j \phi_{n-1} \pm u_k \phi_n) \exp(-2\pi i E t/h) \qquad (20)$$

where $$E = E_k + (n+\tfrac{1}{2})\hbar w_p \pm V(n,p)$$
$$= E_j + (n+1+\tfrac{1}{2})\hbar w_p \pm V(n,p) \qquad (21)$$

These functions are obviously steady states of the combined system, and their energies are eigenvalues of the matrix H. Indeed, once we have stated the problem in the way we have done here, we could have written down the solutions (20) and (21) intuitively. It may be as well to emphasize again the essential difference between the present treatment and previous attempts

* The vectors k and j also have to be parallel to the vector p in wave-number space to get this simple relationship.

to describe electron-phonon interactions. For example in Bardeen's theory of superconductivity (1) the elastic waves were thought of simply as time dependent perturbations of the lattice potential, the lattice points being treated classically and actually performing the oscillatory motion of a point in the classical simple harmonic fashion. Likewise Fröhlich (2), although he recognized the fundamental importance of the resonance between electrons and phonons as such, also accepted the classical picture of the vibrational perturbations, and used the transition probabilities (i.e. emission matrix) calculated in the standard fashion from time-dependent perturbation theory. In the present paper we have instead treated the normal coordinates of the lattice vibrations quantum mechanically, so that instead of a classical point motion we have a wave function for each normal mode coordinate. A pure phonon state of the lattice now is represented not by a pattern of classical motions of the lattice points, but by a spectrum of wave functions, one to each normal coordinate. From this point of view it is quite natural that the potential interaction between electron and phonons should turn out to be a series of possible eigenvalues rather than a continuous function of the time.

As mentioned in the Introduction, the eigenfunctions (20) are states in which one quantum of phonon energy passes back and forth between the electron and the phonons. At no time can one give a definite assignment of energy to the electron alone, nor to the phonon alone; but the total energy is fixed all the time and the state is steady, its normalization being

independent of time. There is a similar state for each normal mode of the lattice, and each such state is quite independent of the excitation of the other normal modes of the lattice. This last point is of course essential to the whole argument: it arises from the orthogonality of the oscillator wave functions used for setting up the V-matrixxin eq.(14), and is achieved only because we have used a completely quantum mechanical treatment of the phonon modes. In a classical treatment of the phonon perturbations one could conceivably achieve a steady state of an electron in a phonon state consisting of one single excited mode, but the presence of other modes - even if only in their lowest zero-point energy states, would constitute an additional time-dependent perturbation and destroy the original state.

In the present theory the state of a combined electron-phonon system could be formed from any linear combination of functions such as (20) with one function to each normal mode:

$$\Psi = \sum_p A_p \Psi_p \qquad (22)$$

A state of zero net current is obtained if both solutions (both signs) and the corresponding functions added for each mode. The net current in any one state like (20) is easily shown to be a mean value between the currents corresponding to the electron states u_k and u_j.

Adiabatic Approximation using Wannier Functions

By contrast with the foregoing exact and completely quantum mechanical treatment we now present an approximate discussion of the electron alone in a time-perturbed lattice potential, using the Wannier functions (3) for the unperturbed states of the electron in the lattice. The difference between the approximate theory and the exact treatment serves to bring out more strongly the significance of the latter.

From the Bloch modulated free-electron wave functions $u_k(q)$ we form the Wannier function over one Bloch zone:

$$U(q, Q_\beta, \{k\}) = N^{-\frac{1}{2}} \sum_k e^{-ikQ_\beta} u_k(q)\, e^{-iE_k t/\hbar} \tag{23}$$

where Q_β is the position of the β^{th} lattice point. We now consider the perturbation potential due to the lattice vibration of a single frequency w and wavelength 2L/p:

$$V_p(q,t) = V_p \sin(\pi pq/L) \sin wt \tag{24}$$

We now make what might be termed a quasi-adiabatic approximation, and assume that the wavelength is extremely long compared with the lattice spacing, and replace the potential (24) by the point function

$$V_p(Q_\beta, t) = V_p \sin(\pi Q_\beta p/L) \sin wt \tag{25}$$

defined only in the neighborhood of any one lattice point. We then form linear combinations of the Wannier functions with variable constants

$$\Psi = \sum_\beta U(q, Q_\beta, \{k\}) \exp\left\{(iV_p/\hbar w) \sin(\pi pQ_\beta/L) \cos wt\right\} \tag{26}$$

We observe at once that this function satisfies the Schrödinger equation

$$i\hbar\,\partial\Psi/\partial t = H_0\Psi + V_p(Q,t)\Psi = H\Psi \qquad (27)$$

where H_0 is the Hamiltonian corresponding to the unperturbed lattice, and $V_p(Q,t)$ can now be written $V_p(q,t)$ without appreciable error. The fact that the Wannier function $U(q, Q_\beta, \{k\})$ has a sharp maximum at the lattice point Q_β permits the potential term to be written in the form appearing in eq.(27) on the present adiabatic approximation.

The nature of this solution, (26), of the Schrödinger equation is clearly a steady state because its square modulus is independent of time. The energy however is not independent of time, but oscillates with the phonon frequency, and therefore it is not an eigenfunction of the Hamiltonian. The solution is only approximate because of the step from eq. (24) to (25), a step that is essential to being able to operate on (26) by H_0 without considering the potential term in the exponent.

The utility of this approximate solution is that it permits us to use the Slater method (4) of perturbations with the Wannier functions. An additional potential perturbation can now be superposed on the phonon potential, for example a simple potential gradient that can again be translated into a point function defined only at the lattice points:

$$V = -eEq \longrightarrow -eEQ_\beta \qquad (28)$$

and the perturbed wave function becomes

$$\Psi = U(q, Q_\beta, \{k\}) \exp\left[(1/i\hbar)\int_0^t V_p(Q_\beta, t')dt' + eEQ_\beta t\right] \qquad (29)$$

We can now use the Slater theorem on the coefficients of this function and calculate the current by means of the formula

$\frac{1}{2}ih\left[\sigma(q)\partial\overline{\sigma}(q)/\partial q - \overline{\sigma}(q)\partial\sigma(q)/\partial q\right]$ where $\sigma(q)$ means the exponential factor in eq.(29). This current has two parts, one the oscillatory current due to the V_p term, and the other a continually increasing current of magnitude $s\Xi t$, thus proving that the phonon perturbed lattice offers no resistance to within the approximations of the present method.

From the point of view of general theory it is essential to go through the exact treatment given in the first part of this paper, to prove that the phonon modulation of a lattice does not cause resistance; the approximate discussion of this section however may yield important practical means of applying the theory to actual crystals.

Conclusions

The implications of this theory are fairly obvious and quite far reaching. The understanding of superconductivity is tied up with the need for a revision of the theory of resistance. The pure coherent phonon states have no resistance. The random transitions among phonon states induced by thermal fluctuations do cause resistance. At sufficiently low temperatures some of the higher phonon modes must drop into their lowest states with zero-point energy. It is then conceivable that under suitable circumstances, the energy available in thermal fluctuations may become too low to excite these modes from their lowest states. In such a case a resonance can occur between electron and zero-point phonon modes, leading to just such current-carrying states as described in this paper. This would not completely explain superconductivity, because the diamagnetic problem remains, but it would account for the transition between normal and superconducting states.

In previous work (5) it was speculated that random changes of phase in the phonon waves were responsible for resistance, and that an order-disorder transition in the phases was responsible for the transition. In the light of the present results it may be that both phase coherence and absence of energy changes among some of the phonon modes are needed for superconductivity. In any case considerable light will be cast on this question by a detailed discussion of transitions among the phonon modulated electron states, and this will be undertaken in a later paper.

References

1.	J.Bardeen	Physical Review, 79, 167-8, Jy 1, 1950 Physical Review, 80, 567-74, Nov.15, 1950 Rev. Mod. Phys., 23, 268-70, Jy. 1951
2.	H.Fröhlich	Physical Review, 79, 845-56, Sept.1, 1950 Proc. Phys. Soc. Lond.A63, 778 Jy. 1950 Proc. Phys. Soc. Lond.A64, 129 Feb. 1951
3.	G.H.Wannier	Physical Review, 52, 191, 1937
4.	J.C.Slater	Physical Review, 76, 1592, Dec.1 1949
5.	W.Band	Physical Review, 79, 739 and 1005, 1950 National Bureau of Standards Circular 519, Oct. 1952